LONG-TERM WATER-QUALITY CHARACTERISTICS

OF CHARLOTTE HARBOR, FLORIDA

By Thomas H. Fraser, Environmental Quality Laboratory, Inc., Port Charlotte, Florida

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 86-4180

Prepared in cooperation with the

FLORIDA DEPARTMENT OF ENVIRONMENTAL REGULATION

Contract Number: ER-90422

Name of Contractor: Environmental Quality Laboratory, Inc.

Principal Investigator: Thomas H. Fraser

Contract Officer's Representative: Benjamin F. McPherson

Short Title of Work: Long-Term Water Quality Effective Date of Contract: August 13, 1984 Contract Expiration Date: September 30, 1984

Amount of Contract: \$16,850

Date Report is Submitted: May 30, 1985

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UNITED STATES DEPARTMENT OF THE INTERIOR

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LONG-TERM WATER-QUALITY CHARACTERISTICS OF CHARLOTTE HARBOR, FLORIDA

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ABSTRACT

Water-quality data for nine constituents collected from January 1976 through March 1984 in upper Charlotte Harbor were examined for evidence of trend (change) with time. Average seasonal patterns and moving averages were described to aid initial descriptions of variation. Multilinear regression models were developed using independent variables that are known to or that may affect variation of constituents. A nonparametric analysis (Seasonal Kendall test) was used as a different approach to determine trends. These results were generally consistent with the parametric analyses. Evidence suggested an increasing trend for temperature and orthophosphate and a decreasing trend for near-surface dissolved oxygen. The temperature trend was related to low winter temperatures early in the period. The orthophosphate trend was related to a major source, the Peace River. The source of the dissolved oxygen trend was not identified, but a relation with primary producers (phytoplankton) was likely. Evidence of a trend was not found for total phosphate, reactive silica, and organic nitrogen. Trend analysis for chloride appeared complicated by strong serial correlation, and the tentative conclusion was that no trend occurred. Nitrate plus nitrite and ammonia data contained too many values that were less than detection limits, and trend analysis could not be made.

INTRODUCTION

A number of published studies describe the water quality of Charlotte Harbor (see Stoker and Karavitis, 1983, who also include many unpublished reports). One general account (Taylor, 1974) summarizes much of the previous water-quality information. None of the published papers, either prior to the Taylor report or since, have examined water-quality data for the occurrence of trends.

Dragovich and others (1968) presented some of the best early data on the harbor and the relations between water quality and biological productivity. Fraser (1981) presented some evidence that fish abundance was linked to freshwater inflow and seasonal water-quality changes, particularly in the wet season. Fraser and Wilcox (1981) described the response of primary producers in Charlotte Harbor to seasonal pulses of nutrients. Frolich and others (1985) provided evidence of biological activity along the salinity gradient and speculated about coastal influence of estuarine discharges. These and other studies cited link biological responses with chemical and physical water-quality parameters in Charlotte Harbor.

Purpose and Scope

The purpose of this report is to describe the presence or absence of change in some of these major chemical and physical parameters during an 8-year period at a fixed location (station 9) in upper Charlotte Harbor (fig. 1). Among the parameters examined for trends, temperature, chloride (salinity), and dissolved oxygen are important determinants of estuarine biological activity. Inorganic nutrient levels of orthophosphate, reactive silica, ammonia, and nitrate-nitrite can determine rates of primary production and influence the kinds of algae present in the water column. Organic nitrogen is a source of inorganic nitrogen when remineralized and may also be a partial measure of living biomass in the water column.

The principal approach used to analyze this 8-year data set was relatively simple in theory. A multilinear regression model was developed that adjusts for various known effects, such as a flow-concentration or concentration-concentration relation, and cyclical effects, such as seasons or tidal components. Any changes that were strongly related with time after such independent variables are included were considered to be strong evidence of a trend. Many of the potential issues, such as data fit by a normal distribution, multicollinearity of independent variables, and nonrandom patterns of error residuals, including their autocorrelation, were assessed. A second approach was used for some data sets with serially correlated error residuals. These data sets were subjected to autoregression analysis as a variation of the ordinary least-squares regression analysis. A third approach used to analyze the data sets involved the use of a nonparametric procedure, the modified Seasonal Kendall test. This procedure makes no assumptions about distribution pattern of the data. Consistency of the nonparametric procedure with the other techniques produces additional support for conclusions that trends exist.

Acknowledgments

I thank William Sanders, University of Tennessee, and James R. Slack, U.S. Geological Survey, Reston, Va., for discussions concerning treatment of the data and trend analyses. Comments on a draft manuscript were made by Edward R. German, U.S. Geological Survey, Orlando, Fla., and James R. Slack.

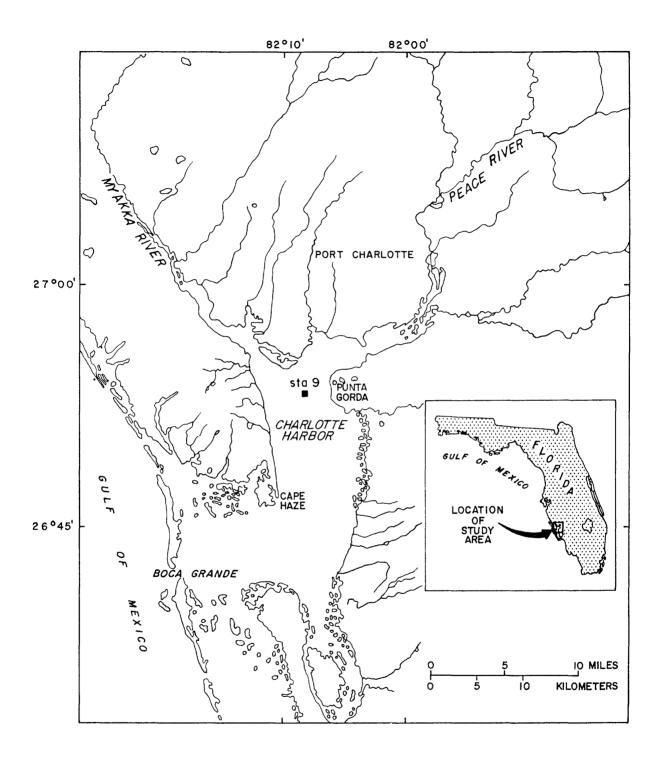


Figure 1.--Environmental Quality Laboratory sample site, station 9, in Charlotte Harbor, Fla., near marker 1.

METHODS OF STUDY

Chemical and Physical Measurements

All chemical and physical measurements for the study were made by staff of the Environmental Quality Laboratory, Inc.

Temperature was measured using an <u>in situ</u> thermistor-type probe. The probe had a consistent bias when water temperatures were above 27 $^{\circ}$ C and read lower than a standard thermometer. This bias also appeared in plots of error residuals versus predicted values for the regression models. Readings above 30 $^{\circ}$ C may be low by as much as 0.4 $^{\circ}$ C. Corrections were not applied to the data to adjust for this bias.

Chloride concentration was measured by the argentometric technique (American Public Health Association, 1980) and was converted to salinity by multiplying 1.806 times chloride in grams per liter. This method for estimating salinity in an estuary is subject to error at low chloride values.

Dissolved oxygen (D0) was measured with a temperature-compensated, passive polarographic cell with gold and silver electrodes. This cell was covered with an oxygen-permeable membrane and filled with a potassium chloride solution. Water-saturated air was used to calibrate the probe to within ±0.1 mg/L (milligram per liter). Partial pressure of oxygen in water was converted to parts per million by the instrument. Values were corrected for salinity effect using the formula:

$$D0 = measured D0 \times 1 - 0.003333 \times conductivity$$
 (1)

All values were from in situ measurements made near the surface or near the bottom. Variation due to time of day was ignored in this analysis.

The calculation of saturation was based on the formula given by Kester (1975, p. 562). To obtain percent saturation, the probe-corrected, dissolved-oxygen reading in milligrams per liter was converted to a volume (milliliters per liter) and then was divided by the calculated saturation value. The equation used for probe-corrected readings was:

$$V = (D0/32) \times 22.385 \frac{T + 273}{273}$$
 (2)

where

V = dissolved oxygen, in milliliters per liter;

T = temperature, in degrees Celsius; and

DO = probe-corrected value, in milligrams per liter.

Orthophosphate was measured using the U.S. Environmental Protection Agency (EPA) (1979) chemical method 365.3, a colorimetric ascorbic acid process. Water samples were unfiltered, cooled to 4 °C, and analyzed within 24 hours. The minimum detection limit was about 0.005 mg/L.

Total phosphate was measured using EPA (1979) chemical method 365.3, a colorimetric ascorbic acid process. Digestion of orthophosphate is done using an acid persulfate solution. Otherwise, the method is the same as for orthophosphate. The minimum detection limit is about 0.010 mg/L.

Reactive silica was measured using EPA (1979) chemical method 370.1 with a minimum detection limit of 0.005 mg/L. Water samples were unfiltered, cooled to $^{\circ}$ C, and analyzed within 24 hours.

Nitrate plus nitrite was measured using EPA (1979) chemical method 353.2, a colorimetric, automated cadmium reduction process. Water samples were unfiltered, cooled to 4 $^{\circ}$ C, and analyzed within 24 hours. Between January 1976 and October 1977, the minimum detection limit was 0.01 mg/L. Beginning in November, this was decreased to 0.003±0.003 mg/L. Values were reported as N.

Ammonia was measured using EPA (1979) chemical method 350.1, a colorimetric, automated phenate process with a minimum detection limit of about 0.001 mg/L. Water samples were unfiltered, cooled to 4 °C, and analyzed within 24 hours. All data prior to January 1978 were discarded as unreliable or erroneous because the method was not sufficiently correcting for a salt effect. An adjustment was made in the method after January 1978. Values were reported as N.

Organic nitrogen is the calculation of total Kjeldahl nitrogen (TKN) minus ammonia. TKN was measured by using EPA (1979) chemical method 351.1, a colorimetric, automated phenate process. Water samples were digested at high temperature with a sulfuric acid-potassium sulfate mixture in the presence of a selenium catalyst. The resulting ammonia was measured as per method 350.1. All data prior to May 1979 were discarded as unreliable or erroneous because of an analytical problem that was corrected in May 1979. Organic nitrogen was reported as N.

Water samples were collected at 2-week intervals from January 1976 through June 1977. From July 1977 through March 1984, samples were collected monthly. Additional data were collected in June 1982 and February 1983 during unusually high flows in the Peace River. <u>In situ</u> measurements were made at the same time the water samples were collected.

Data Analysis

Raw data were inspected both from computer output of distributional characteristics and graphical displays with time to check for any remaining errors and for descriptive purposes. Paired t-tests of near-surface versus near-bottom data were used to determine whether these sample locations represented different or the same levels of concentration. Seasonal or annual changes of the various constituents were described from raw data plots, moving averages, and the annual average for 8 years of data. The presence or absence of systematic change for a water-quality characteristic involved examination of raw data plots, 3-month and 5-month moving averages, and the development of multilinear models with a time variable.

Statistical procedures within the SAS Institute, Inc., 1982, system were used to estimate parameters and test hypotheses of parameters included in regression models. Observed error residuals were examined with respect to predicted values and time. Systematic error in the residuals was reduced, where possible, to random error by using predetermined independent variables. Diagnostics were used to eliminate those variables that showed multicollinearity and, thus, decreased the reliability of the slope for any time trend. Autocorrelated errors may affect tests of hypotheses, particularly those that have marginal probability to be accepted as significant.

Simple Fourier functions were used to represent various cyclical changes (such as seasonal on tidal variables) that may affect the respective water-quality characteristic. The cyclical changes were not measured. The simple Fourier functions were expressed as paired sine and cosine oscillations. One to three functions were used: a 365-day cycle, a 182.5-day cycle, and a 3.232.5-day cycle. All of these cycles were divided into 2π . Sine-cosine pairs were entered together, and pooled F values were examined for significance (table 1). These variables were entered after measured variables and were retained only if significant and if they exhibited low multicollinearity with other variables.

Frequently, the sine-cosine pair will have only one-half of the pair contributing to the model and the other providing little explanation. This may be the result of the relatively simple physical cycles that the sine-cosine pair is substituted for instead of real data. Occasionally, one-half of the sine-cosine pair for the 3,232.5-day cycle will be strongly collinear with the time variable and also not provide significant additional explanation of a model (see orthophosphate model for January 1976-March 1984). In such latter cases, the offending half of the pair was omitted.

Independent variables were predetermined for each constituent examined and all variables were added at once. The order of variables for models was first those measured variables at station 9, then measured variables in the region of Charlotte Harbor, and finally Fourier functions in order of most simple cycle to most complex. Time was the last variable in each model. Variables that did not contribute to the model or were collinear with other variables were then omitted. The slope of the time coefficient was then tested to determine if its slope was different from zero.

Seasonal Kendall test procedures with the SAS system were used as outlined in Crawford and others (1983). Tests were made on the raw data and on variable adjusted data output of error residuals. Fvidence for trend was accepted if the probability of the Kendall's tau value was less than or equal to 0.1.

¹Use of the trade name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1.--Pooled sine and cosine functions by regression model with F values, degrees of freedom (DF), and level of significance (p) for each cycle

Water-quality	Pool	ed F va	lues		p = 0	.05 for	larger F
parameter	for cy	cles, i	n days	DF	for	cycles,	in days
model			3,232.5		365		3,232.5
Temperature							
Тор	439.0	_		2, 112	Yes	_	-
Bottom	580.07	-	~	2, 112	Yes	-	-
Chloride							
Tcp	-	14.29	_	2, 119	_	Yes	_
Bottom	8.43		-	2, 119	Yes	Yes	-
Dissolved oxygen							
Bottom	_	4.66	-	2, 112	-	Yes	-
Orthophosphate							
Тор							
Jan. 76-Mar. 84	38.01	19.27	43.62	2, 118	Yes	Yes	Yes
Jan. 76-July 78	14.15	9.06	_	2, 48	Yes	Yes	_
Aug. 78-Apr. 82	33.98	4.86	3.85	2, 42	Yes	Yes	Yes
Mar. 82-Mar. 84	40.40		_	2, 24	Yes	Yes	_
Bottom				-,			
Jan. 76-Mar. 84	61.04	5.86	30.19	2, 117	Yes	Yes	Yes
Jan. 76-July 78	16.20	_		2, 48	Yes	Yes	Yes
Aug. 78-Apr. 82	29.94	5.44	.03	2, 41	Yes	Yes	No
Mar. 82-Mar. 84	35.17	7.33	-	2, 24	Yes	Yes	_
Total phosphate							
Top	20.15	4.47	13.19	2, 107	Yes	Yes	Yes
Bottom	45.03	_	2.02	2, 108	Yes	_	No
Silica							
Top	50.91	_		2, 119	Yes	_	_
Bottom	87.15			2, 119	Yes		

RESULTS OF STATISTICAL ANALYSES

Multilinear Regression Analysis

Temperature

The range of water temperature was 21 $^{\circ}$ C (11 $^{\circ}$ C to 32 $^{\circ}$ C near bottom, 11.5 $^{\circ}$ C to 32.5 $^{\circ}$ C near the surface) for 261 observations. A paired t-test, based on the differences between near surface and near bottom, indicated the upper layer warmer (p = 0.0001) by about 0.55 $^{\circ}$ C+0.92 $^{\circ}$ C. Water temperature was less than 20 $^{\circ}$ C for about 25 percent of the observations. This estuary, therefore, may be characterized as having subtropical temperatures with predominantly tropical characteristics for much of the year.

Both near-surface and near-bottom average monthly temperatures were very similar. Only December, January, and February averaged below 20 °C. Average water temperature was above 28.5 °C from June through September and peaked in July (fig. 2). Warming and cooling rates appeared about the same for the 3 months before and after the high summer values and the low winter values in January and February.

Moving averages of both near-surface (fig. 3) and near-bottom temperatures over the 8 years showed an increase in the low winter temperature that was interrupted only during the winter of 1980-81. Peak summer temperatures appeared variable with no pattern.

Wind and a harmonic function used as a proxy for light were the only independent variables included in the model. Average air temperature was not used because heat transport to and from Charlotte Harbor by climatic conditions (number and strength of cold fronts) should provide the variation from year-to-year that may result in a trend. The effects of heat exchanges as the result of cooler or warmer water from either the Gulf of Mexico or the tidal river were ignored. The values for wind were a 7-day average of measurements from the Fort Myers Airport NOAA (National Oceanic and Atmospheric Administration) station. Light was assumed to vary as a simple sine-cosine function over the year $(2\pi/365)$. This harmonic cycle may also include other seasonal variables such as temperature. A trend for increasing temperature was suggested based on model estimates (tables 2, 10, and 12). Karl and others (1984) noted that the continental United States had three colder than normal winters from 1976-77 through 1978-79. This pattern was reflected in the moving averages at station 9 and lead to an interpretation that winter temperatures have been warming since the winter of 1976-77 in an apparent systematic fashion. The basis for the trend may be simply that the period started with three unusually cool winters followed by four warm winters out of five.

The equations (table 2) suggest that a 7-day average, 10-mi/h wind would reduce temperature by about 3 °C. This is reasonable because the average wind speeds tended to be less than 7 mi/h from June through September (except for tropical disturbances) and greater than 7 mi/h during November through May. Frontal activity during November through May caused these high wind speeds. Frontal activity was frequently accompanied by lower temperatures and higher barometric pressures.

Salinity

The range of salinity was 34.5 $^{\circ}$ /co (parts per thousand) (0.5 to 35.0 $^{\circ}$ /co) near surface and 29.0 $^{\circ}$ /co (8.7 to 37.7 $^{\circ}$ /co) near bottom for 122 observations. A paired t-test based on the differences between near-surface and near-bottom values was significant (p = 0.0001) with the near surface less salty by about 2.47±3.82 $^{\circ}$ /co. Only 25 percent of the readings were less than 19.8 $^{\circ}$ /co near surface and 22.4 $^{\circ}$ /co near bottom. Most of the time, this area of the harbor was nearly 20 $^{\circ}$ /co or greater, averaging 23.1 $^{\circ}$ /co near surface and 25.6 $^{\circ}$ /co near bottom.

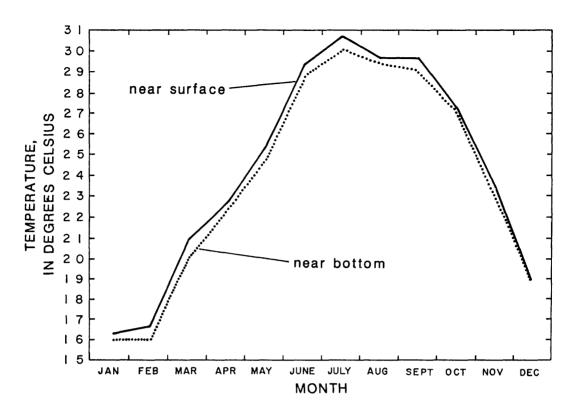


Figure 2.—Average monthly near-surface and near-bottom temperature, January 1976 through March 1984.

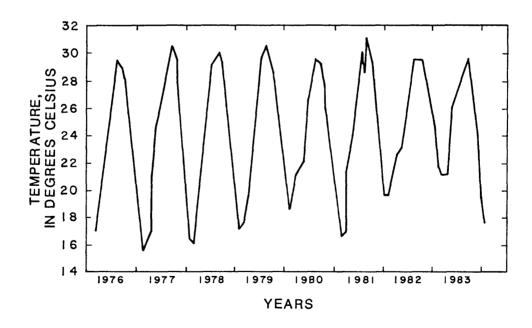


Figure 3.—Three-month moving average for near-surface temperature, January 1976 through March 1984.

Table 2. -- Multilinear regression models for temperature at station 9

[The t statistic under each coefficient is in parentheses. N is the number of observations, and R² is the amount of explained sum of squares. Temperature is in degrees Celsius, wind is in miles per hour, and time (t) is consecutive numbers beginning January 1, 1960]

	N	R2
SURFACE		
Temperature = $21.02 - 0.334$ (wind) - 2.836 (sin $2\pi/365 \times t$) - 5.630 (cos $2\pi/365 \times t$) (13.92) (-3.12) (-9.96)	115	0.87
+ 4.875x10 ⁻⁴ (t) (3.62)		
BOTTOM		
Temperature = $21.44 - 0.288$ (wind) - 3.059 (sin $2\pi/365 \times t$) - 5.688 (cos $2\pi/365 \times t$) (16.03) (-3.03) (-12.11)	115	. 90
$+ 5.643 \times 10^{-4} \text{ (t)}$ (3.13)		

All salinity data were measured as chloride concentration and the following analyses are presented as chloride in milligrams per liter rather than as salinity in parts per thousand. Figure 4 shows the average monthly chloride concentration for near-surface and near-bottom water. Near-surface chloride declined from maximum concentration in May to the minimum concentrations in September (fig. 4). Near-bottom chloride concentration behaved similarly except the decline began in June. A slight dip in chloride levels occurred during the dry season from February through April. The monthly changes in chloride were the result of changes in freshwater inflow, principally from the Peace River.

Moving averages for chloride did not reveal a regular seasonal change (fig. 5). The low point each year was less than the preceding year through 1979, and less than all previous years in 1982 and 1983. This may indicate a decreasing trend. High chlorides in the dry years of 1977 and 1981 were the result of low rainfall and freshwater inflow.

The model for chloride has as independent variables the 7-day average flow from the seaward most gaged stations in the Peace River basin, annual cycle in sea level, and the effects of flushing differences between equinoxes and solstices. The latter two are expressed as simple sine-cosine functions $(2\pi/365 \text{ and } 2\pi/182.5)$. A decreasing trend for salinity was evident based on model estimates (tables 3 and 10). The reason for this trend was probably the increasing freshwater inflows during 1976 through 1979 and the high inflows in 1982.

At flows of 100 ft³/s, the near-surface model predicts chloride levels of 20,777 mg/L (37.5 %)/oo salinity), which is relatively close to the maximum value observed, indicating that the coefficients appear reasonable. The near-bottom model is about the same at 20,798 mg/L (37.6 %)/oo salinity) for a 100-ft³/s flow.

Dissolved Oxygen

The range of concentration for dissolved oxygen was 7.9 mg/L (4.3 to 12.2) in near-surface water and 9.4 mg/L (0.1 to 9.5) in near-bottom water. A paired t-test based on the differences between near-surface and near-bottom values was significant (p = 0.0001), with near-surface water having about 2.6 ± 2.4 mg/L more oxygen. Twenty-five percent of all observations were less than 6.9 mg/L (near surface) and 3.4 mg/L (near bottom). Ten percent of the near-bottom values were 0.9 mg/L or less. Only 1.5 percent of the near-surface values were less than 5.0 mg/L.

Near-surface average oxygen values declined from about 8.5 to 6.7 mg/L from January to July and then began rising again (fig. 6). The small spike (increase) in September may be the result of low salinities and increased phytoplankton productivity. Near-bottom values peaked in February, declined slowly through May, and then declined more rapidly to July. The low near-bottom values (less than 3 mg/L) during summer were attributed to restricted reaeration as a result of density stratification and to biological respiration. A sharp increase in dissolved oxygen concentration occurred from October to December.

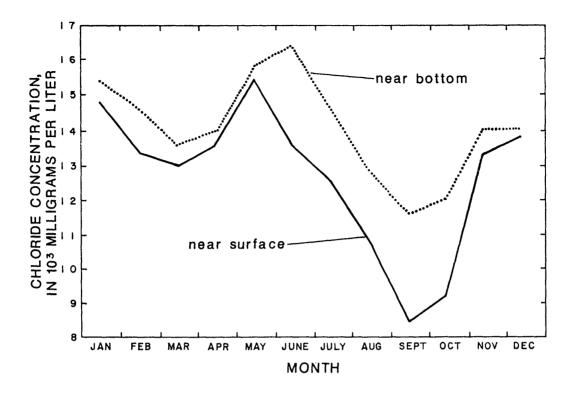


Figure 4.--Average monthly near-surface and near-bottom chloride concentration, January 1976 through March 1984.

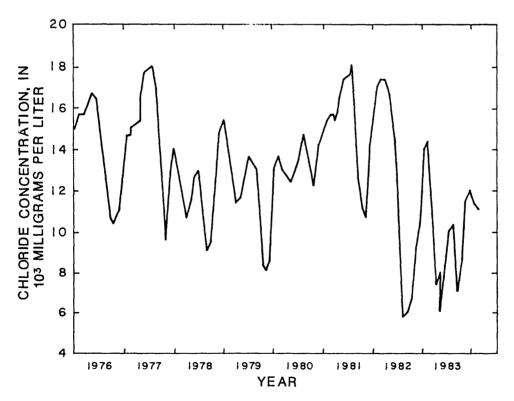


Figure 5.--Three-month moving average for near-surface chloride concentration, January 1976 through March 1984.

Table 3.--Multilinear regression models for chloride at station 9

N is the number of observations, and \mathbb{R}^2 is the amount of explained sum of squares. Chloride is in milligrams per liter, average flow is ir natural logarithms of cubic feet per second, and time (t) is in consecutive numbers beginning January 1, 1960] [The t statistic under each coefficient is in parentheses.

.56 H2 122 122 z Chloride = 32,639.45 - 2,575.5 (flow) + 827.21 (cos $2\pi/182.5$ x t) + 479.24 (sin $2\pi/182.5$ x t) Chloride = 26,629.65 - 1,339.03 (flow) - 604.22 (cos $2\pi/365 \times t$) + 137.35 (sin $2\pi/365 \times t$) -0.4904(t)(-2.53)(1.80)(0.51)251.11 (sin $2\pi/182.5 \times t$) (-2.42)(96.0)(3.22)+ 997.98 (cos 2n/182.5 x t) -(-7.69)(-16.03)- 0.3668 (t) (-1.81)(21.25)(4.07)(17.5)SURFACE BOTTOM

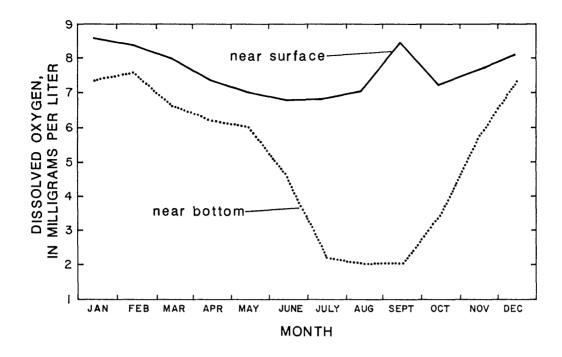


Figure 6.—Average monthly near-surface and near-bottom dissolved oxygen, January 1976 through March 1984.

A 3-month moving average for the 8 years showed a declining trend in near-surface dissolved oxygen (fig. 7). The 3-month moving average for near-bottom dissolved oxygen had a more regular seasonal pattern than the near-surface moving average (fig. 8). The near-bottom moving average showed a decline in the winter peak values from 1977 through 1982. No high peaks occurred during the winters of 1980-81 and 1981-82 in near-surface dissolved oxygen, unlike the near-bottom moving average.

The model for near-surface oxygen (table 4) that accounted for most variation was one that included temperature, salinity, and chlorophyll <u>a</u>, all variables that affect the amount of oxygen present in water. Although not collected as part of this study, chlorophyll <u>a</u> was included in one of the models to illustrate the importance of biological activity in the near-surface water. This model, along with the other model using only temperature and salinity (tables 4 and 10), indicated decreasing dissolved oxygen with time.

There was no trend in dissolved oxygen for near-bottom values after accounting for variation due to temperature, vertical stratification, wind stress, and an annual variable representing the sea-level cycle. Unlike the surface model, the bottom model had a very high R value.

Reasons for the declining trend in surface oxygen values are not apparent, but the absence of trend in near-bottom waters suggests that the availability of light and its effect on primary productivity may be involved. In northern Charlotte Harbor, primary productivity may be restricted by light penetration to less than 15.75 inches depth (Ralph Montgomery, Environmental

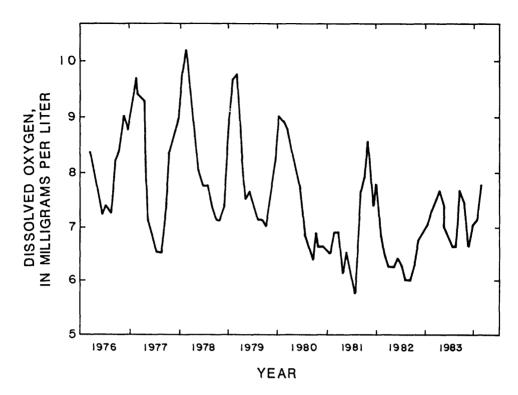


Figure 7.—Three-month moving average for near-surface dissolved oxygen, January 1976 through March 1984.

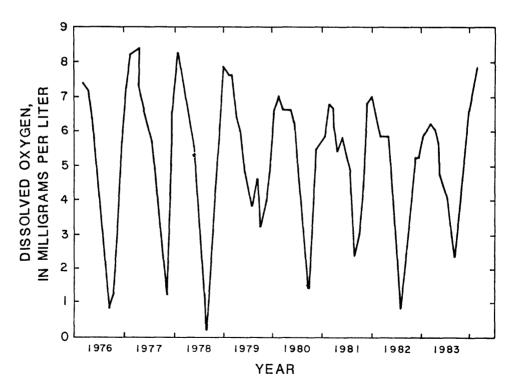


Figure 8.—Three-month moving average for near-bottom dissolved oxygen, January 1976 through March 1984.

Table 4. -- Multilinear regression models for dissolved oxygen at station 9

amount of explained sum of squares. Dissolved oxygen is in milligrams per liter, temperature is in degrees [The t statistic under each coefficient is in parentheses. N is the number of observations, and \mathbb{R}^2 is the miles per hours, $\Delta\sigma\tau$ is difference in specific gravity between surface and bottom water, and time (t) is consecutive numbers beginning January 1, 1960] Celsius, salinity is in parts per thousand, chlorophyll a is in milligrams per cubic meter, wind is in

	Z	R ²
SURFACE		
Dissolved oxygen = $17.83 - 0.154$ (temp) + 0.0191 (Chl <u>a</u>) - 0.0532 (sal) - $7.616x10^{-4}$ (t) (14.68) (-7.54) (4.64) (-3.19) (-5.99)	93	0.54
= $16.39 - 0.126$ (temp) - 0.0811 (sal) - $5.450x10^{-4}$ (t) (15.96) (-6.84) (-5.24) (-5.20)	116	.42
BOTTOM		
Dissolved oxygen = 11.53 - 0.279 (temp) - 0.426 ($\Delta \sigma \tau$) + 0.116 (wind) + 0.0210 (cos $2\pi/182.5 \text{ x t}$) 115 (10.25) (-10.38) (-9.03) (1.67)	t) 115	.81
- 0.3355 ($\sin 2\pi/182.5 \times t$) + 6.155 $\times 10^{-5}$ (t) (2.15)		
SURFACE		
Percent saturation = $184.86 + 0.1602$ (temp) + 0.2912 (Chl a) - 0.1624 (sal) - 0.0106 (t) (10.46) (0.54) (4.84) (-0.67)	93	.38
= 183.69 + 0.3135 (Chl a) - 0.0105 (t) (13.61) (5.70) (-5.77)	93	.38

Quality Laboratory Inc., written commun., 1985). A decrease in primary productivity in near-surface waters would decrease daytime oxygen production and could cause a decreasing trend in dissolved oxygen.

To test this idea, dissolved oxygen in milligrams per liter was converted to milliliters per liter, and percent saturation was calculated based on measured temperature and salinity. If nonbiological activity, such as simple physical factors, was involved, then saturation should be relatively close to 100 percent. About 25 percent of the observations (N = 261) had saturation levels of 102 percent or less, and 50 percent were 111 percent or greater, which suggests that biological activity may be important. Average monthly values also support this idea (fig. 9).

Two multilinear models for percent saturation (table 4) indicated that chlorophyll <u>a</u> was an important variable, whereas temperature and salinity were not. One conclusion that could be drawn from these two models is that a decline in primary productivity may be indicated by a drop in observed percent saturation.

The bottom dissolved-oxygen models predicted 4.5 mg/L of dissolved oxygen at the mean temperature, mean density difference, and mean wind speed. This was close to the average dissolved oxygen value of 5.0 mg/L for near bottom. All other models were poor predictors of average values.

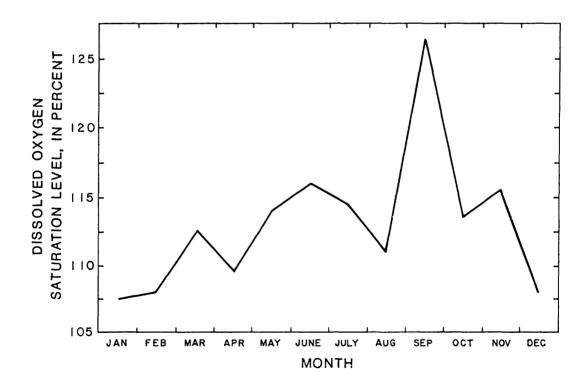


Figure 9.—Average monthly near-surface percent saturation level of dissolved oxygen, January 1976 through March 1984.

Orthophosphate

The range of concentration for orthophosphate as P was 0.59 mg/L (0.07 to 0.66) for 121 samples of near-surface water and 0.62 mg/L (0.07 to 0.69) for 120 samples of near-bottom water. A paired t-test, based on the differences between near surface and near bottom, was significant (p = 0.0001) with the near surface averaging 0.025 ± 0.067 mg/L higher. Seventy-five percent of all values were 0.15 mg/L or greater for both depths, and the lowest value of 0.07 mg/L was probably not low enough to limit primary production.

Monthly average values were similar for both depths (fig. 10). Low near-surface values occurred from October through May with peak values during July through September. The seasonal cycle for orthophosphate coincided with the seasonal flow cycle of the Peace River.

The 3-month moving average of concentration indicated a distinct trend (fig. 11). Annual maximum and minimum values increased each year from 1977 through 1980 for both surface and bottom (not shown). The minimum values from 1979 through 1984 were higher than those from 1976 through 1978 (fig. 11).

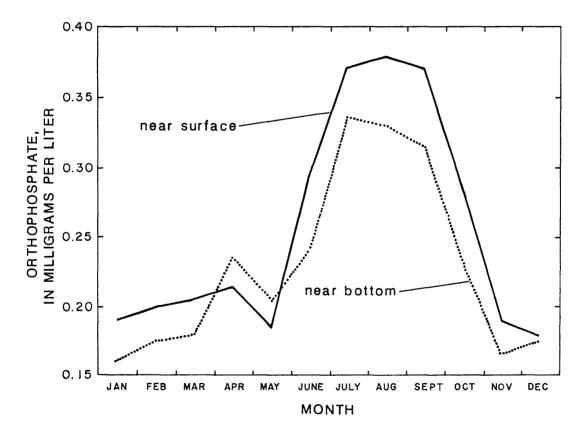


Figure 10.--Average monthly near-surface and near-bottom orthophosphate concentration, as P, January 1976 through March 1984.

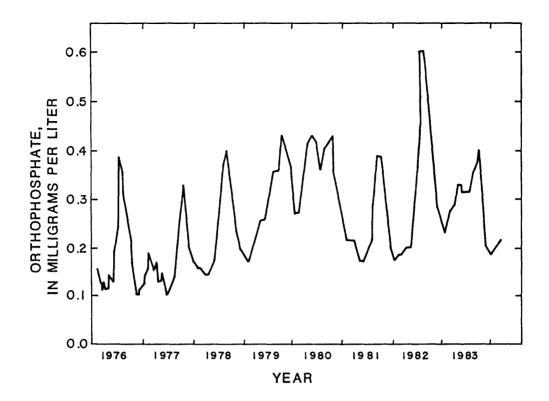


Figure 11.--Three-month moving average for near-surface orthophosphate, as P, January 1976 through March 1984.

Independent variables in the models are chloride (mixing effects of freshwater and saltwater) and the proxies for various cycles [annual sea-level cycle $(2\pi/365)$, tidal flushing effects due to difference between equinoxes and solstices $(2\pi/182.5)$, and change in tidal flushing due to the revolution of perigee $(2\pi/3,232.5)$]. An increasing trend was present and highly significant at both depths for the 8-year data set (tables 5 and 10).

Another more detailed analysis (T. H. Fraser, written commun., 1985) suggested that, in the Peace River, orthophosphate data may be subdivided into a period of no change (January 1976 through July 1978), increasing orthophosphate (August 1978 through April 1982), and decreasing orthophosphate (March 1982 through March 1984). The data at station 9, when examined for these shorter time periods (tables 5 and 6), showed trends similar to those of the Peace River. This suggests that the Peace River was the principal source of the observed trends at station 9. Any model depicting or predicting the distribution of orthophosphate in Charlotte Harbor in the absence of some in situ data could utilize measurements from the Peace River.

Total Phosphate

The range of concentration for total phosphate as P was 0.70 mg/L (0.03 to 0.73) for 110 samples of near-surface water and 0.99 mg/L (0.06 to 1.05)

Table 5.--Multilinear regression models for near-surface and near-bottom orthophosphate at station 9

amount of explained sum of squares. Orthophosphate is in the natural log of milligrams per liter, chloride [The t statistic under each coefficient is in parentheses. N is the number of observations, and \mathbb{R}^2 is the is in milligrams per liter, and time is consecutive numbers beginning January 1, 1960]

R2 z

SURFACE

January 1976-March 1984

Orthophosphate =
$$-1.846 - 6.025 \times 10^{-5}$$
 (C1) -0.2268 (cos $2\pi/365 \times t$) -0.0780 (sin $2\pi/365 \times t$) 121 0.72 (-7.07) (-7.63) (-6.31) (2.05) (2.05) (4.01) (1.74) (4.01) (4.01) (5.98) (5.98)

January 1976-July 1978

Orthophosphate =
$$-0.6422 - 8.5490 \times 10^{-5}$$
 (C1) -0.2592 (cos $2\pi/365 \times t$) -0.059 (sin $2\pi/365 \times t$) 51 .53 (-0.46) (-3.62) (-3.76) (-3.76) (-0.06) + 0.1302 (cos $2\pi/182.5 \times t$) + 0.1794 (sin $2\pi/182.5 \times t$) + 1.1780×10⁻⁶ (t) (1.73)

Table 5. --Multilinear regression models for near-surface and near-bottom orthophosphate at station 9--Continued

	Z	R2
August 1978-April 1982		
Orthophosphate = $-3.694 - 6.5475 \times 10^{-5}$ (C1) -0.2185 (cos $2\pi/365 \times t$) -0.916 (sin $2\pi/365 \times t$) (-2.01)	45	0.78
+ 0.0114 (cos $2\pi/182.5 \times t$) + 0.1058 (sin $2\pi/182.5 \times t$) (0.22)		
+ 0.5203 ($\sin 2\pi/3$,232.5 x t) + 3.919x10 ⁻⁴ (t) (3.66)		
March 1982-March 1984		
Orthophosphate = $2.671 - 5.165 \times 10^{-5}$ (C1) - 0.2044 (cos $2\pi/365 \times t$) - 0.0382 (sin $2\pi/365 \times t$) (-0.98)	27	.91
+ 0.1312 (cos $2\pi/182.5 \times t$) + 0.0846 (sin $2\pi/182.5 \times t$) - 4.025×10^{-4} (t) (3.43)		

Table 5.--Multilinear regression models for near-surface and near-bottom orthophosphate at station 9--Continued

	Z	R2
BOTTOM		i i i
January 1976-March 1984		
Orthophosphate = $-2.015 - 5.183 \times 10^{-5}$ (C1) -0.3031 (cos $2\pi/365 \times t$) -0.0661 (sin $2\pi/365 \times t$) (5.95) (-4.21)	120	09.0
+ 0.339 (cos $2\pi/182.5 \times t$) + 0.0885 (sin $2\pi/182.5 \times t$) (0.80)		
+ 0.2113 ($\sin 2\pi/3$,232.5 x t) + 1.630x10 ⁻⁴ (t) (5.06)		
January 1976-July 1978		
Orthophosphate = $-2.759 - 5.868 \times 10^{-5}$ (C1) -0.3321 (cos $2\pi/365 \times t$) + 0.003784 (sin $2\pi/365 \times t$) (-1.81) (-2.18) (-4.03)	51	.32
+ 2.818x10 ⁻⁴ (t) (1.28)		

Table 5.--Multilinear regression models for near-surface and near-bottom orthophosphate at station 9--Continued

	Z	R ²
August 1978-April 1982		
Orthophosphate = $-2.9400 - 1.108 \times 10^{-4}$ (C1) -0.2211 (cos $2\pi/365 \times t$) -0.0991 (sin $2\pi/365 \times t$) (-2.92) (-3.88) (-4.55)	4	0.69
+ 0.07521 (cos $2\pi/182.5 \times t$) + 0.1182 (sin $2\pi/182.5 \times t$) (1.18)		
$+0.2497 \text{ (sin } 2\pi/3,232.5 \text{ x t)} + 3.947\text{x}10^{-4} \text{ (t)}$ (1.50)		
March 1982-March 1984		
Orthophosphate = $3.835 - 6.089 \times 10^{-5}$ (C1) - 0.3024 (cos $2\pi/365 \times t$) - 0.0475 (sin $2\pi/365 \times t$) (-0.70)	27	.76
$+$ 0.1999 (cos $2\pi/182.5 \times t$) + 0.0758 (sin $2\pi/182.5 \times t$) - 5.296×10^{-4} (t) (2.79) (1.08)		

Table 6.--Summary of shorter time trend slopes within the 8-year period at station 9 for orthophosphate

[N is the number of observations, R² is the amount of explained sum of squares, the time coefficient, and the Autocor-Positive related errors None None None None None statistic Watson-Durbin 1.58 1.33 1.58 2.11 probability (p) of the coefficient being different from zero] relation autocor-.289 order .180 .050 .133 .038 First 0.185 Decreasing Increasing Increasing Decreasing Trend No trend No trend .2065 .0019 .0539 0.9954 .0390 .0080 Ω, $1.1780 \times 10^{-6} \\ 2.818 \times 10^{-4}$ 3.919×10^{-4} 3.947×10^{-4} -4.025×10^{-4} -3.821×10^{-4} Time 0.53 .32 .78 .91 R2 45 44 5151 27 27 Z Mar. 82-Mar. 84 Aug. 78-Apr. 82 Jan. 76-July 78 Bottom ---Surface --Bottom ---Surface ---Surface --Bottom --

for 111 samples of near-bottom water. A paired t-test, based on the differences between near surface and near bottom, was barely significant (p = 0.0984), with the near surface averaging 0.015 ± 0.097 mg/L higher than near bottom. About 90 percent of all values were greater than 0.16 mg/L.

Monthly average values were similar for both depths. Low near-surface values occurred from October through June and high values occurred from July through September (fig. 12). This seasonal cycle was generally consistent with low and high flows in the Peace River. The 3-month moving average of surface concentration does not show any progressive increase or decrease in annual maximum and minimum values (fig. 13).

The models for total phosphate (table 7) included the same independent variables as those for orthophosphate. No trend was indicated for either depth (tables 7 and 10). One might assume a trend in orthophosphate also would result in a trend for total phosphate. However, the moving averages appear different (fig. 11 and fig. 13) with relatively more nonsoluble phosphate (total phosphate minus orthophosphate) in the maxima of 1976, 1977, and 1978 than in subsequent years. A simplistic explanation would suggest that the nonsoluble phosphate variation masked the orthophosphate trend when expressed as total phosphate. Why this may be so is obscure.

Silica

The range of concentration for silica was 3.17 mg/L (0.01 to 3.18) for 122 observations. A paired t-test, based on the differences between near-surface and near-bottom concentrations, was significant (p = 0.0053) with the near bottom greater by about 0.076 ± 0.299 mg/L. Seventy-five percent of all near-surface and near-bottom values were greater than 0.16 mg/L and 0.25 mg/L, respectively. At these levels, silica is likely to limit diatom growth (Werner, 1977).

Both near-surface and near-bottom monthly average concentrations of silica were similar (fig. 14). Concentrations were low between December and May and increased from June to September, with a small decline in August. The higher levels during summer resulted from higher inflows of freshwater rich in silica.

The 3-month moving average of silica showed an annual cycle with no systematic change in the annual maxima or minima (fig. 15). The summer peak of 1981 was less than one-half of the peak 1982. Also, the winter trough of 1982-83 was higher than preceding years.

Independent variables in the models included chloride (diluting effects), an annual cycle (weathering), and for the near-surface model, chlorophyll \underline{a} (indirect measure of algae biomass including diatoms). The time coefficient was not significant, therefore no trend was apparent (tables 8 and 10). The absence of trend for silica may be ascribed to no change in the weathering process that produces soluble silica.

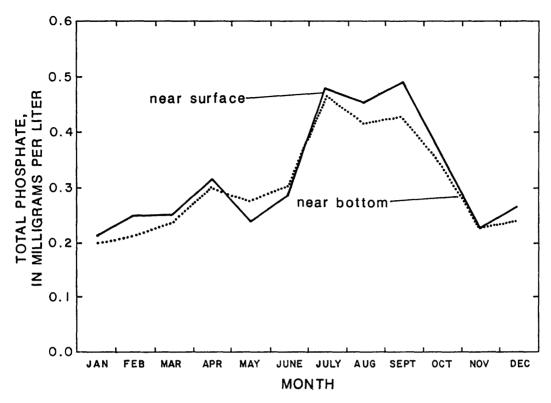


Figure 12.—Average monthly near-surface and near-bottom total phosphate concentration, as P, January 1976 through March 1984.

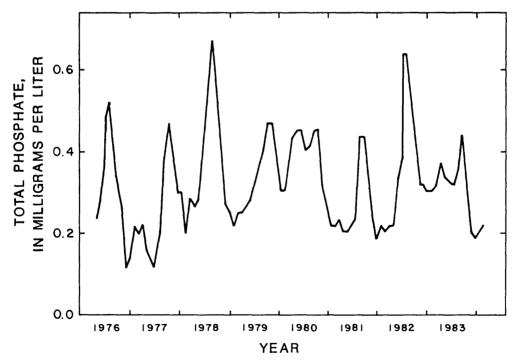


Figure 13.--Three-month moving average for near-surface total phosphate concentration, as P, January 1976 through March 1984.

Table 7. -- Multilinear regression models for total phosphate at station 9

[The t statistic under each coefficient is in parentheses. N is the number of observations, and R is the amount of explained sum of squares. Total phosphate is in the natural log of milligrams per liter, chloride is in milligrams per liter, and time is consecutive numbers beginning January 1, 1960] R2

SURFACE

110 0.52 Total phosphate = $-0.663 - 6.822 \times 10^{-5}$ (C1) - 0.1996 (cos $2\pi/365 \times t$) - 0.1125 (sin $2\pi/365 \times t$) (-4.11)(-1.86) (-6.10)

+ 0.0200 (cos $2\pi/182.5 \text{ x t}$) + 0.1087 (sin $2\pi/182.5 \text{ x t}$) (0.38)

+ 0.1914 (sin $2\pi/3$,232.5 x t) + 3.510x10⁻⁵ (t)

BOTTOM

.46 111 Total phosphate = $-0.774 - 4.411x10^{-5}$ (C1) - 0.3169 (cos $2\pi/365 \times t$) - 0.1350 (sin $2\pi/365 \times t$) (-2.57) (-6.14)(-3.04)(-1.85)

 $+0.0734 \text{ (sin } 2\pi/3,232.5 \text{ x t)} + 1.120 \text{x} 10^{-5} \text{ (t)}$

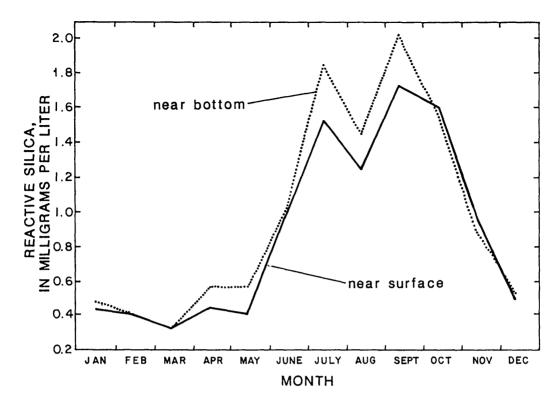


Figure 14.—Average monthly near-surface and near-bottom reactive silica concentration, as Si, January 1976 through March 1984.

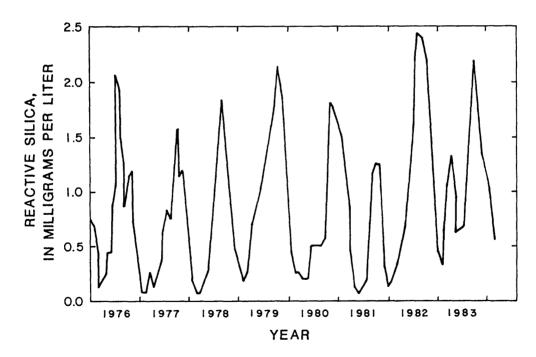


Figure 15.--Three-month moving average for near-surface reactive silica concentration, as Si, January 1976 through March 1984.

Table 8.--Multilinear regression models for silica at station 9

amount of explained sum of squares. Silica is in milligrams per liter, chloride is in milligrams per liter, chlorophyll a is in milligrams per cubic meter, and time is consecutive numbers beginning January 1, 1960] [The t statistic under each coefficient is in parentheses. N is the number of observations, and \mathbb{R}^2 is the

	Z	R2
SURFACE		
Silica = 1.494 - 9.424x10 ⁻⁵ (Cl) + 3.155x10 ⁻³ (Chl <u>a</u>) - 0.4133 (sin $2\pi/365 \times t$) (2.68) (-6.84) (1.52) (5.61)	76	0.65
- 0.2209 (cos $2\pi/365 \times t$) + 3.785×10 ⁻⁵ (t) (-3.14) (0.55)		
= $1.629 - 9.004 \times 10^{-5}$ (C1) - 0.4026 (sin $2\pi/365 \times t$) - 0.2861 (cos $2\pi/365 \times t$) (3.49) (-6.67) (5.80)	122	.58
$+5.375 \times 10^{-5}$ (t) (1.01)		
BOTTOM		
Silica = $2.028 - 8.689 \times 10^{-5}$ (Cl) - 0.509 (sin $2\pi/365 \times t$) - 0.4548 (cos $2\pi/365 \times t$) (3.39) (-4.15) (-6.74)	122	.52
$+ 2.053 \times 10^{-5} (t)$ (0.34)		

Nitrate Plus Nitrite

A significant portion of the nitrate plus nitrite data collected after October 1977 (N = 157) was represented by "less than" values (N = 62). For purposes of this analysis, values at the method detection limits were treated as real (absolute) measurements. This overestimates actual nitrate plus nitrite concentrations. Ninety-five percent of all concentrations were less than 0.101 mg/L for near-surface samples collected after October 1977 and less than 0.054 mg/L for near-bottom samples collected after October 1977. Average near-surface monthly values were highest in April and October (fig. 16).

Analysis for a time trend is not presented because of the large number of "less than" values. Nitrate and nitrite are readily usable sources of nitrogen for phytoplankton and may be in short supply because of biological demand.

Ammonia

Eighty-eight of the 145 observations of ammonia (as N) were below the detection limits. The average detection limit for near-surface data was 0.015 ± 0.016 mg/L, with a range of 0.0001 to 0.097 (N = 51). For purposes of this analysis, these "less than" values were treated as real (absolute) measurements. This overestimates actual values. Ninety percent (N = 130) of all concentrations since January 1978 were less than 0.27 mg/L for near-bottom

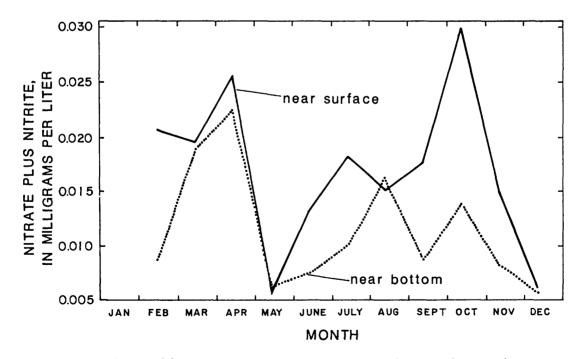


Figure 16.--Average monthly near-surface and near-bottom nitrate plus nitrite concentration, as N, for a 6-year period.

samples and less than 0.11 mg/L for near-surface samples. Monthly averages suggested that near-bottom levels of ammonia were much greater than near-surface levels from June through October (fig. 17). Most near-bottom ammonia concentrations from June through October were above detection limits.

Analysis for a time trend is not presented because of the large number of "less than" values. A probable reason for the low ammonia concentrations was uptake by phytoplankton.

Organic Nitrogen

The range of organic nitrogen (as N) was 2.30 mg/L (0.12 to 2.40) for 59 observations. A paired t-test, based on the concentration differences between near-surface and near-bottom values, was significant (p = 0.021) with the near-surface waters greater by about 0.10 mg/L.

Both near-bottom and near-surface average concentrations were similar except for an obvious peak in the near-surface average in September (fig. 18). Monthly variation was low from November through March, but a secondary peak occurred in April (fig. 18). The 3-month moving averages did not show discernible trends (figs. 19 and 20).

Independent variables utilized in the models included chloride (mixing effects of freshwater and saltwater), chlorophyll \underline{a} (indirect measure of algae biomass), and total organic carbon (a measure of all organic material). Neither model indicated a trend with time. The surface model had a much higher R value (tables 9 and 10) than the bottom model.

Autoregression Analysis

The use of an autoregression term was added to those models showing a time trend and also having significant autocorrelated errors (Durbin-Watson Statistic, tables 11 and 12). These models were specified with the addition of a new term (the previous value) lagged not less than a 14-day or greater than a 31-day interval. The reason for using an autoregressive approach was that the tests of significance may be affected because the standard errors may be different between this process and ordinary least-squares. For example, both temperature and chloride measurements are likely to be influenced by the preceding measurement and, therefore, to some extent may cause the autocorrelated errors.

Table 12 provides the results of autoregressive models for temperature, orthophosphate, and chloride. The total number of observations was reduced more than one in table 12 because the lag term must fall within a specified time period. The autocorrelated errors that were significant in table 11 became nonsignificant when the lag terms were introduced in table 12. In those models for which the autoregressive terms were not significant (table 11), there were no changes in the significance of the time trend for temperature

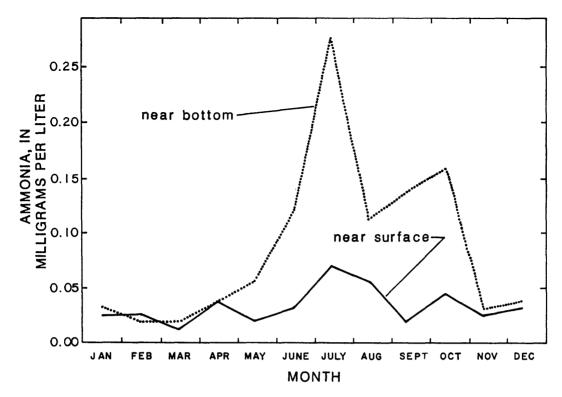


Figure 17.—Average monthly near-surface and near-bottom ammonia concentration, as N, for a 6-year period.

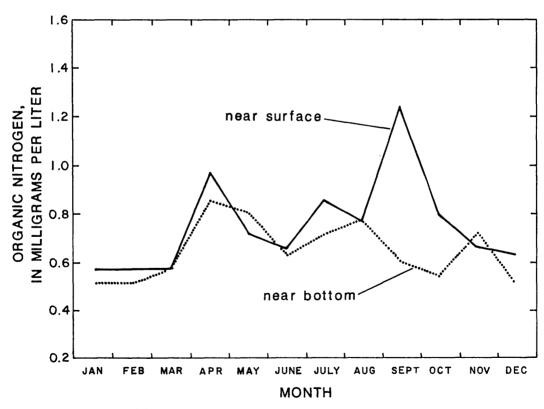


Figure 18.--Average monthly near-surface and near-bottom organic nitrogen concentration, as N, for a 4.5-year period.

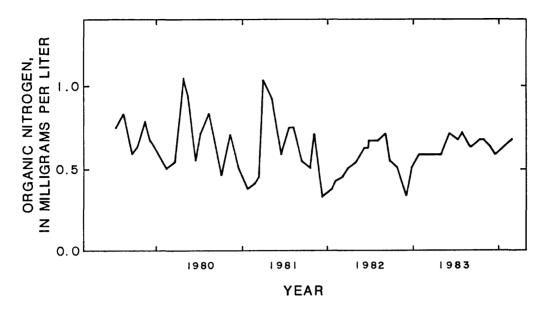


Figure 19.--Three-month moving average for near-surface organic nitrogen, as N, May 1979 through March 1984.

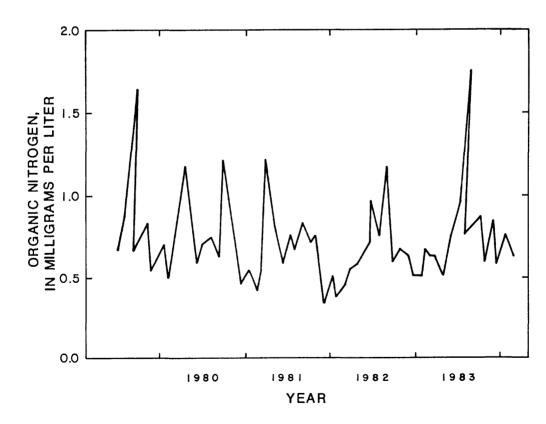


Figure 20.--Three-month moving average for near-bottom organic nitrogen, as N, May 1979 through March 1984.

Table 9. -- Multilinear regression models for organic nitrogen at station 9

amount of explained sum of squares. Organic nitrogen is in milligrams per liter, chlorophyll a is in milligrams per cubic meter, total organic carbon (TOC) is in milligrams per liter, chloride is in milli-[The t statistic under each coefficient is in parentheses. N is the number of observations, \mathbb{R}^2 is the grams per liter, and time is consecutive numbers beginning January 1, 1960]

	Z	N R ²
SURFACE		
Organic nitrogen = $0.922 + 6.661x10^{-3}$ (Chl <u>a</u>) - $3.153x10^{-5}$ (Cl) + $7.398x10^{-6}$ (t) (1.77) (6.55) (-3.83) (0.12)	28	58 0.62
BOTTOM		
Organic nitrogen = $1.545 - 1.031 \times 10^{-2}$ (TOC) - 2.596×10^{-5} (C1) - 4.444×10^{-5} (t) (2.46) (-1.86) (-2.18)	26	56 .14
		1

Table 10.--Summary of the time trend slopes for the 8-year period at station 9

[N is the number of observations, R² is the amount of explained sum of squares, the time coefficient, and the probability (p) of the coefficient being different from zero]

	N	R ²	Time	P	Trend
Temperature					
Surface	115	0.8739	4.785×10^{-4}	0.0002	Increasing
Bottom	115	.8995	5.643×10^{-4}	.0022	Increasing
Chloride			•		
Surface	122	.7508	-3.668×10^{-1}	.0733	Decreasing
Bottom	122	.5612	-4.904×10^{-1}	.0128	Decreasing
Dissolved oxygen			,		
Surface (without Chl <u>a</u>) -	116	.4248	-5.450×10^{-4}	.0001	Decreasing
(with Chl <u>a</u>)	93	.5387	$-7.616 \times 10_{-5}^{-4}$.0001	Decreasing
Bottom	115	.8119	6.155×10^{-3}	.6057	No trend
Percent oxygen saturation					
Surface	93	.3824	0105	.0001	Decreasing
Orthophosphate					
Surface	121	.7159	1.575×10^{-4}	.0001	Increasing
Bottom	120	.6003	1.630×10^{-4}	.0001	Increasing
Total phosphate			c		
Surface	110	.5184	3.510×10^{-5}	.3830	No trend
Bottom	111	.4642	1.120x10 ⁻³	.7921	No trend
Silica			r		
Surface (without Chl <u>a</u>) -	122	.5798	5.375×10^{-3}	.3136	No trend
(with Chl <u>a</u>)	97	.6485	3.785×10^{-3}	.2734	No trend
Bottom	122	.5190	2.053×10^{-3}	.7317	No trend
Organic nitrogen					
Surface	58	.6212	7.398×10^{-6}	.9046	No trend
Bottom	<u>56</u>	.1400	$-4.444x10^{-3}$.5155	No trend
Surface Bottom Silica Surface (without Chl <u>a</u>) -	111 122 97 122	.4642 .5798 .6485 .5190	1.120x10 ⁻⁵ 5.375x10 ⁻⁵ 3.785x10 ⁻⁵ 2.053x10 ⁻⁶	.7921 .3136 .2734 .7317	No trend No trend No trend No trend

and orthophosphate (table 12). When the autoregressive terms were significant, for example chloride, there were changes in the significance of the time trends. These results may indicate that a decreasing trend for chloride did not occur after including the previous chloride level.

Table 11.--Summary of first-order autocorrelated errors for each multilinear model with evidence for a time trend given in table 10 at p = 0.05

N	is	the	number	of	observations	l
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	N	First order autocorrelation	Durbin-Watson statistic	Autocorrelated errors
Temperature				
Surface	115	0.139	1.70	None
Bottom	115	.268	1.44	Positive
Chloride				
Surface	122	.275	1.43	Positive
Bottom	122	.489	1.01	Positive
Dissolved oxygen				
Surface	116	.058	1.85	None
Bottom	92	.046	1.87	None
Percent saturation	93	.023	1.92	None
Orthophosphate				
Surface	120	.310	1.32	Positive
Bottom	118	.155	1.67	Indeterminate

Seasonal Kendall Analysis

All data except nitrate-nitrite and ammonia were subjected to a modified nonparametric analysis (Crawford and others, 1983; Hirsch and Slack, 1984) for trends. The citations listed above provide reasons for using such a test when analyzing water-quality data. Perhaps the most important reason for using a nonparametric test is a lack of dependence on specific theoretical distributions. The results have been divided into two tables (13 and 14) based on the presence or absence of a trend from the multilinear regression analysis (tables 10 and 11).

All constituents were examined as simple (untransformed) data (tables 13 and 14) and as residuals of the multilinear regression analyses, excluding any Fourier functions and the time variable. These error residuals were then subjected to the Seasonal Kendall test and the results shown under the "adjusted" heading (tables 13 and 14).

There were differences in the results between the adjusted residuals and the measured data for temperature, dissolved oxygen, chloride (all table 13), organic nitrogen, and silica (table 14). The adjusted Seasonal Kendall tests for trend agreed well with the multilinear regressions for all constituents except chloride (table 15). Test results of the simple (untransformed) data

Table 12. -- Autoregressive analysis of the water-quality variables with significant autocorrelation terms for models specified in tables 2, 3, and 5 at p = 0.05

[N is the number of observations, R² is the amount of explained sum of squares, the time coefficient, and the probability (p) of the coefficient being different from zero]

	Z	First order autocor- relation	Durbin- Watson statistic	Autocor- related errors	R ²	Time	Ω,	Trend
Orthophosphate SurfaceBottom	9 <i>L</i>	-0.185	1.61	None	0.70	1.144x10 ⁻⁴ 1.728x10 ⁻⁴	0.0085	Increasing Increasing
Temperature Surface	77	.028	1.94	None None	. 90	8.574x10 ⁻⁴ 6.355x10 ⁻⁴	.0006	Increasing Increasing
Chloride SurfaceBottom	76	081	2.14	None None	.80	2634	.1594	None None

Table 13.--Summary of nonparametric Seasonal Kendall test for constituents in table 11

[N is the number of seasonal values (one set per month). T is a modified form of Kendall's tau and its probability (p) of the tau value not indicating a change with time. Slope is the trend magnitude measured as the median of the slopes of ordered pairs of data. Adjusted data are error residuals from multivariate models. Fourier functions were not used in adjusting the data]

	N	T	p	Slope	Trend
Temperature					
Surface	97	0.159	0.056	0.1150	Increasing
Bottom	97	.130	.119	.0535	No trend
Adjusted					
Surface	96	.232	.006	.3801	Increasing
Bottom	96	.250	.003	.3526	Increasing
Chloride					
Surface	97	139	.100	-232.7	Decreasing
Bottom	97	176	.036	-195.0	Decreasing
Adjusted					
Surface	97	040	.650	-35.3	No trend
Bottom	97	145	.087	-158.6	Decreasing
Orthophosphate					
Surface	97	.329	.001	.0685	Increasing
Bottom	96	.328	.001	.0660	Increasing
Adjusted					
Surface	97	.191	.023	.0359	Increasing
Bottom	96	.213	.012	.0446	Increasing
Dissolved oxygen					
Surface	97	379	.001	2225	Decreasing
Bottom	97	179	.033	1115	Decreasing
Adjusted					· ·
Surface	97	434	.001	2169	Decreasing
Bottom	96	.024	.805	.0152_	No trend

did not agree with tests of residuals in 5 of the 14 tests. No consistent reason was apparent; however, two results (temperature and chloride) were at probability levels close to or at the 0.10 level of acceptance. Crawford and others (1983) noted that, when serial correlation of the observations occur, the actual significance may be twice the reported level for monthly data. Such serial correlations may occur for those constituents (temperature, chloride, orthophosphate) treated in the autoregression analysis (also see table 11).

Table 14.--Summary of nonparametric Seasonal Kendall test for constituents with no trends in table 10

[N is the number of seasonal values (one set per month). T is a modified form of Kendall's tau and its probability (p) of the tau value not indicating a change with time. Slope is the trend magnitude measured as the median of the slopes of ordered pairs of data. Adjusted data are error residuals from multivariate models. Fourier functions were not used in adjusting the data]

	N	T	р	Slope	Trend
Total phosphate					
Surface	94	0.108	0.215	0.0214	No trend
Bottom	95	061	.493	.0034	No trend
Adjusted					
Surface	94	086	.325	0018	No trend
Bottom	94	085	.330	0194	No trend
Silica					
Surface	97	.194	.021	.0574	Increasing
Bottom	97	.107	.209	.0326	No trend
Adjusted					
Surface	97	.058	.508	.0203	No trend
Bottom	97	.046	.601	.0154	No trend
Organic nitrogen					
Surface	56	.229	.078	.0476	Increasing
Bottom	56	.210	.107	.0395	No trend
Adjusted					
Surface	56	.048	.760	.0082	No trend
Bottom	56	.124	.359	.0155	No trend

DISCUSSION

The analyses for presence or absence of trends in the 8-year data set at station 9 involved several approaches: raw data display, computerized reduction and inspection of the distributional characteristics of the raw data, determination of moving averages, and application of various regression models. The 3-month moving averages appeared to have a distinct seasonal variation as a result of freshwater inflow from the Peace River. Regression and autoregressive models were used to provide estimates of trends with time as an independent variable. Resulting slopes were then tested against the hypothesis that the time slope was not equal to zero; that is, a time trend existed (table 10).

The nonparametric approach to trend analysis gave results that agreed very well with parametric procedures. This agreement suggests that strong conclusions can be made for the presence or absence of long-term monotonic trends for all constituents except chloride (table 15).

Table 15.--Summary of indications of trend utilizing multilinear regression, autoregression, and Seasonal Kendall analyses

[n.a. = not applicable]

	Multilinear regression	Auto- regression	Adjusted Seasonal Kendall	Trend comment
Temperature				
Surface	Yes	Yes	Yes	All increasing
Bottom	Yes	Yes	Yes	All increasing
Chloride				
Surface	Yes	No	No	Probably no trend
Bottom	Yes	No	Yes	Probably no trend
Dissolved oxygen				
Surface	Yes	n.a.	Yes	Both decreasing
Bottom	No	n.a.	N_{O}	No trend
Orthophosphate				
Surface	Yes	Yes	Yes	All increasing
Bottom	Yes	Yes	Yes	All increasing
Total phosphate				
Surface	No	n.ə.	N_{O}	No trend
Bottom	No	n.ə.	No	No trend
Silica				
Surface	No	n.a.	N_{O}	No trend
Bottom	No	n.a.	No	No trend
Organic nitrogen				
Surface	No	n.ə.	N_{O}	No trend
Bottom	No	n.a.	No	No trend

First-order autocorrelation of the errors was examined for those constituents that showed evidence of a trend to determine the presence of significant correlations (table 11). Those models with marginal probability of being accepted as significant and having a significant autocorrelation of errors may result in accepting a trend when one is not present. This situation appears possible for the chloride models.

Chloride (salinity) trend probably does not occur after adjusting the data for freshwater inflow. After adjusting for inflow, it is likely that only some geomorphological change, such as a dam on the river or changing the cross section of Boca Grande Pass, would permit more or less salt to enter the estuary, thus changing the mixing relations at station 9. The highly significant lagged chloride term in the autoregressive model and the autocorrelated errors in the multilinear model may indicate the greater degree of

serial correlation in time for the chloride data than any other constituent examined. This issue clouds the interpretation of statistical results for both parametric and nonparametric analyses.

The results for both temperature and orthophosphate indicate the trends are identifiable for both parametric and nonparametric analyses. Temperature changes that appeared systematic (fig. 3) occurred only during the winter months, causing lower temperatures to persist longer in the colder years (compare the winter of 1976-77 with 1979-80). Orthophosphate trends, although showing the effects of some seasonality (fig. 11), do exhibit supra-annual increases (compare high and low points from late 1977 through 1980). These changes were related to changes observed in the discharge of this constituent from the Peace River. The source of this material was from above Arcadia, and the trends were of such magnitude as to suggest that a relation exists with the economic conditions of the phosphate mining and fertilizer industry.

Dissolved-oxygen trends clearly were different between surface and bottom, probably because stratification during the wet season inhibited mixing. The decreasing trend in near-surface dissolved oxygen may be related to changes in primary production by phytoplankton. This is given some support because concentration of chlorophyll <u>a</u>, a measure of phytoplankton biomass, correlated with the decreasing dissolved oxygen values. The presence of a decreasing trend in the surface water is of some concern and should be investigated at other stations to determine if this trend is more widespread.

CONCLUSIONS

Trends

- 1. Temperature and orthophosphate showed increasing trends at a station in upper Charlotte Harbor during the 8-year period. The cause of the temperature trend appeared to be low winter temperatures early in the period that resulted from large-scale meteorological events. Increasing orthophosphate was the result of changes related to a major source, the Peace River.
- 2. Dissolved oxygen decreased in near-surface waters during the 8-year period but showed no change in near-bottom waters. The cause of the surface decline was obscure, but some indications suggest a relation with primary producers (phytoplankton).
- 3. Changes were not found for organic nitrogen, reactive silica, and total phosphate. As the result of some ambiguity, salinity showed real changes with time (moving averages), but when modeled using flow and a lagged salinity, no trend appeared, which suggests that freshwater inflow and saltwater mixing relations have not changed during this period at the station.
- 4. Ammonia and nitrate plus nitrite were in such low supply (mostly below detection limits) as to preclude an analysis for a trend.

Seasonality

- 1. Temperature, salinity, orthophosphate, total phosphate, and reactive silica all had seasonal patterns that were similar near the surface and near the bottom.
- 2. Dissolved oxygen had a different seasonal pattern near the surface compared with near the bottom. This difference was related to biological activity and vertical density stratification.
- 3. In the nitrogen series, only near-bottom ammonia values showed a seasonal pattern. The near-bottom ammonia pattern was related to biological activity and vertical stratification.

Areal coverage

1. Analyses at one station were useful as an initial approach. Identification and explanation of trends, however, may be limited by a single-station approach. Trends for some constituents, like dissolved oxygen, could be different at other stations.

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